RAPID PYROLYSIS OF NEW BRUNSWICK OIL SHALE

Final Report

by

A.P. Watkinson, G-K. Khoe and T. Tam
Department of Chemical Engineering
The University of British Columbia
Vancouver, B.C. V6T 1W5

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SUMMARY

Pyrolysis of New Brunswick oil shale was studied in two 0.15 m dia. spouted bed reactors. The majority of the experiments were done in an electrically heated unit which contained sand spouted by a hot mixture of 15% CO_2-85% N_2. Oil shale of 0.5-1.0 mm, 1-2 mm, and 2-4 mm size was fed into the reactor at about 1.5 kg/h. Oil was recovered from a slip stream of the reactor off gases. The oil yields and elemental oil composition were determined as a function of reactor temperature (450-550°C), particle size, and feed rate. The optimum temperature for pyrolysis of the 1-2 mm shale was about 475°C at which oil yields of 89% of the Fischer Assay were reached. Coarser particles gave better results reaching in excess of 90% of the Fischer assay. The magnitude of the yield values must be tempered with some caution as oils were found to contain about 5% unaccounted for material which may be oxygenated species. Solvent contamination has been ruled out. Higher feed rates of 3 kg/h were found to decrease the oil yield. Tests in the two stage pyrolysis unit in which pyrolysis occurred in reducing gases generated by sub-stoichiometric combustion of propane showed that there is considerable potential to operate at higher shale feed rates of 4 kg/h and still achieve 89% of the Fischer Assay yield. During operation with the spouted bed considerable attrition of the oil shale occurred. Further work is required to evaluate most suitable operating conditions for a spouted bed oil shale retorting process.

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1. Introduction

Oil shales can be processed in a number of types of retorting units. In the conventional moving bed unit raw shales of size 5-75 mm pass downward through preheating, retorting, combustion and cooling zones. Residence times are of the order of 4-6 hours. Oil yields are about 90% of the Fischer Assay values. In a typical indirectly heated unit such as the TOSCO process, oil yields are around 93% of Fischer Assay.

The general objectives of this work were to determine oil yields and composition for New Brunswick oil shales processes in a rapid pyrolysis unit originally designed for coal. The detailed objectives included a study of of the effect of temperature, feed rate and particle size on the yield and chemical composition of liquid products arising from pyrolysis in a spouted bed unit. The spouting gas was to be either a nitrogen or a nitrogen-carbon dioxide mixture typical of a combustion flue gas produced by burning spent oil shale. Appendix A lists the objectives and tasks of the present research.

Two different spouted bed units were availale for this study. An electrically heated single stage unit shown in Figure 1 and described in Table 1 was used for most of the work. Here the retorting gases were supplied from cylinders. Figure 2 shows a second unit which was used for a few tests. It is a two-stage unit with an upper pyrolysis stage, and a lower combustor unit which is designed to operate autothermally. Spent carbonaceous solids which overflow the upper pyrolysis chamber can be burned in the lower refractory-lined combustor to provide the peat for the endothermic pyrolysis process. The lower stage can be operated under neutral or slightly reducing conditions. In the present work propane rather than spent shale was burned in the lower stage. Steam is used to temper the

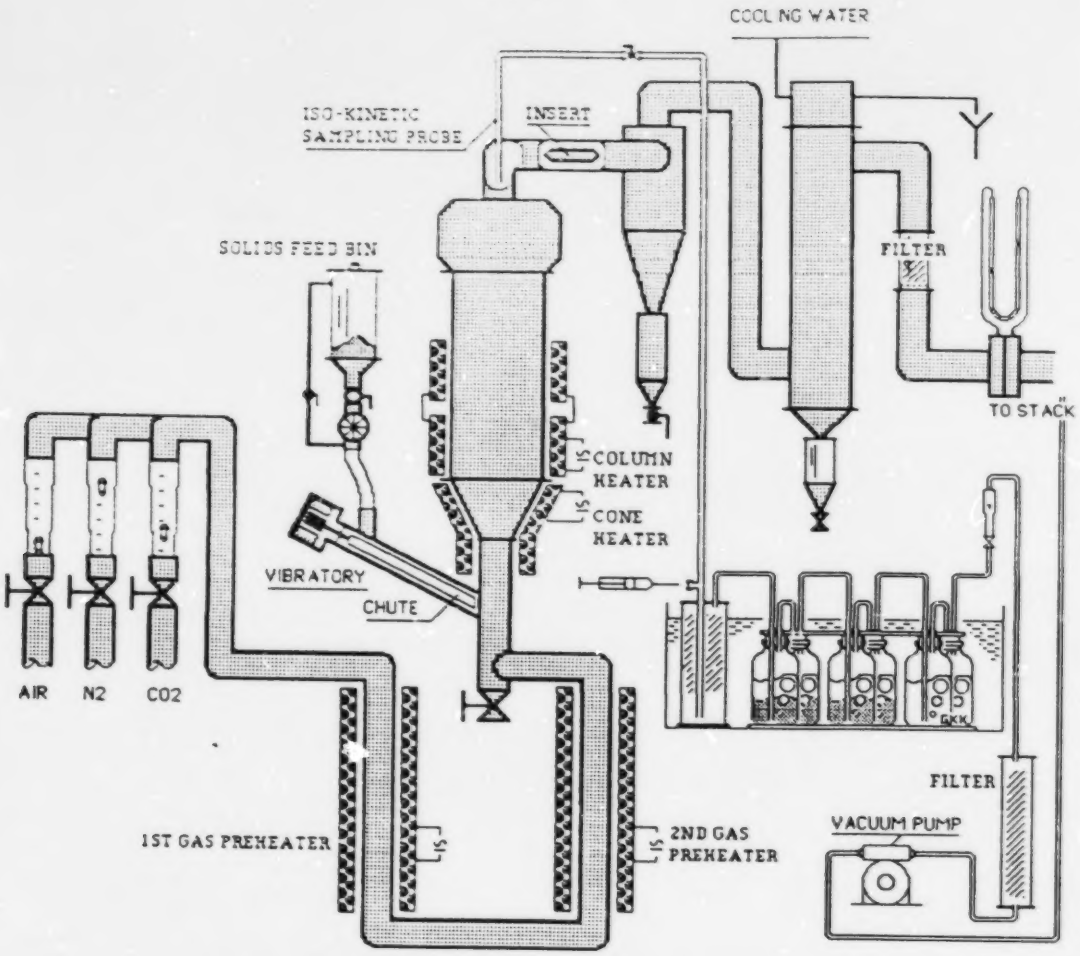


Fig. 1 The electrically heated single stage spouted bed pyrolyzer.

Table 1: Design Characteristics of Electrically Heated Spouted Bed Pyrolyzer System

Reactor:	Material - 317 Stainless Steel Inside diameter - 128 mm Wall Thickness - 6.6 mm Cone Angle - 70° Disengaging section diameter - 255 mm Height (includes cone and disengagement section) - 1.22 m
Gas-Solid Cyclone:	Material - Stainless Steel Diameter - 150 mm Cylinder Height - 500 mm Cone Height - 300 mm
Condenser:	Shell - 316 Stainless Steel Inside Diameter - 128 mm Wall Thickness - 6.6 mm Tubes: 6 U-tubes .86 m long Diameter - 12.7 mm Area = 4130 cm^2
Tar Receiver:	Material - Glass and stainless steel Inside Diameter - 22.9 cm Height - 30.5 cm
Tar Filter:	102 x 305 mm QVF glass column
Orifice Plate:	Material - Stainless Steel Diamter of Orifice - 19.1 mm

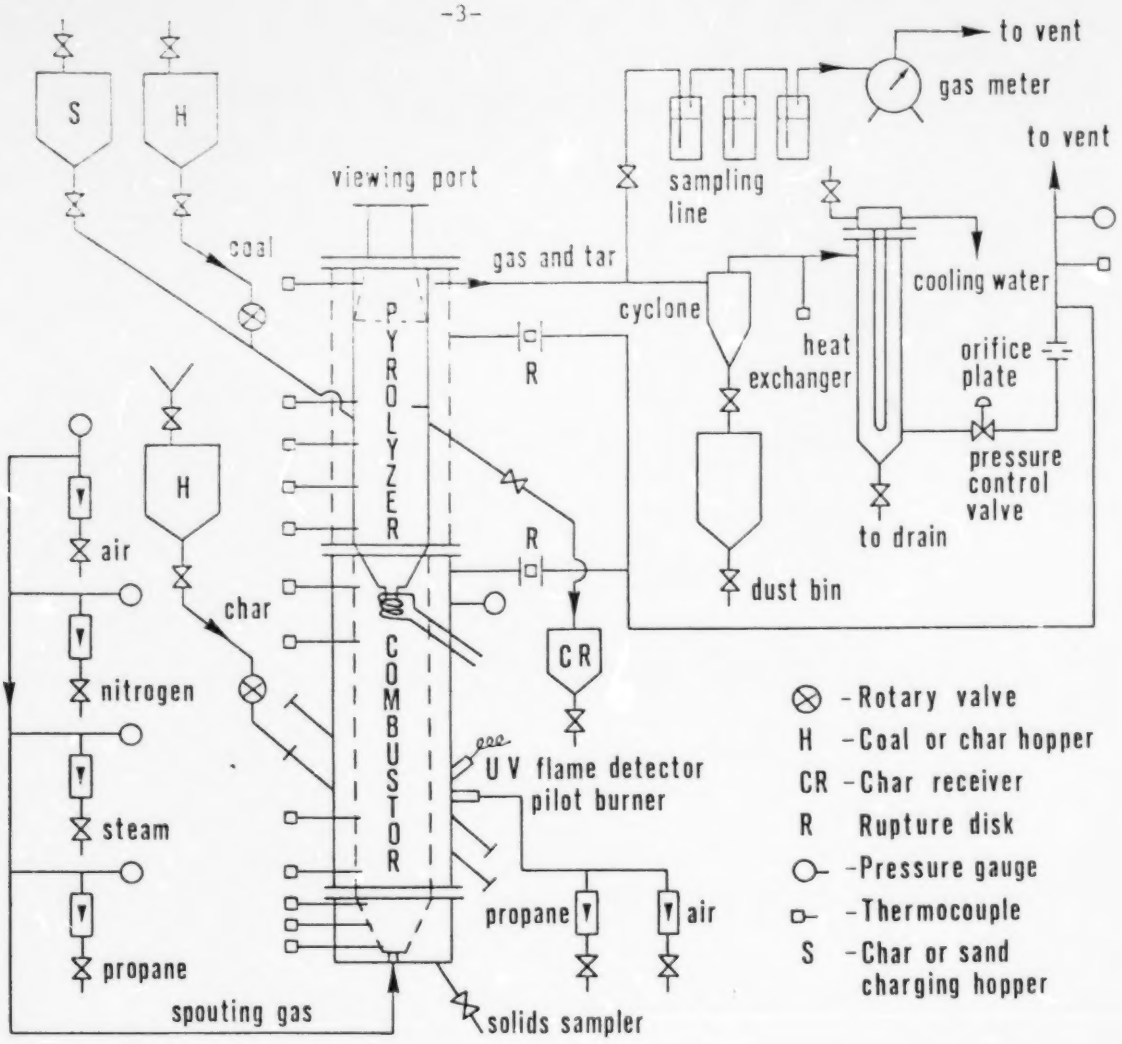


Fig. 2 Schematic of Two-Stages Combustor-Pyrolyzer Unit

Table 2: Design Characteristics of Two-Stage Pyrolyzer Unit

Combustion Section	Steel construction with alumina refractory lining Inside diameter - 0.159 m Cone angle - 60° Orifice diameter - 19.1 mm Cylindrical section height - 1.5 m Pilot propane burner On-line oxygen sensor
Interstage Section	Cast iron core with orifice 19.1 mm Cooling coil with air on the tube-side
Pyrolyzer Section	Type 304 stainless steel - 0.154 m inside dia. x 1 m high Equipped with overflow line
Fixed System	Rotary valve with gearbox and Graham transmission
Condenser	Identical to that in Table 1.

combustion process and an interstage cooler provides further flexibility in temperature control of the pyrolyzer.

2. Oil Shale Properties

Two separate lots of oil shale were supplied by the Research and Productivity Council of New Brunswick.

The original coarse oil shale as received, was reduced in size using a jaw crusher. The minimum gap was set at 0.89 mm and a non-flooding feeding mode was applied, which gave optimum yield of the required size fractions while minimizing waste undersize production.

Avg. Particle Size [mm]	<0.5	0.5-1.0	1.0-2.0	2.0-4.0	>4.0
Yield [wt%]	17.9	10.3	20.3	39.5	11.9

The two lots labelled A and B had different physical appearance, and were kept separate.

Table 3 gives the proximate and ultimate analyses of a blended sample of Oil Shale A. Of note are the ash level of 72.5% and volatile content of 25.2%. Carbon was found to be about 15.9%. In Table 4 the inorganic fraction of the different size fractions of Oil Shale A is analyzed and the organic and inorganic carbon reported. Carbon sulphur and the loss on ignition increase with the average particle size, while the main inorganics decrease. Table 5 lists the modified Fischer Assay results for both shales. Oil Shale A generally is higher in oil yield at about 5.2-7.9% versus 2.9-4.5% for Oil Shale B. Both oil shales give better oil yields from the larger size fractions. Some thermogravimetric analysis results are reported in Section 5(j).

3. Spouting of Oil Shales

To process oil shales in a spouted bed some knowledge of spouting properties is required.

Table 3: Proximate and Ultimate Analysis of Blend of Oil Shale A

Proximate		Ultimate (Dry Basis)	
% Moisture	1.69	% C	15.91
% Ash	72.53	% H	2.05
% Volatiles	25.17	% N	0.51
% Fixed Carbon	0.61	% S	0.92
	100.00	% Cl	0.01
		% Ash	73.78
		% Oxygen (dif))	6.82
			100.00

Table 4: Analysis* of Oil Shale Ash and Carbon

Size Fraction (mm)	0.5-1.0	1-2	2-4
Total Organic Carbon (%)	10.2	10.6	12.4
Total Carbon (%)	12.3	13.3	14.7
SiO_2 (% wt)	43.4	41.9	41.6
Al_2O_3	10.6	10.4	10.3
Fe_2O_3	4.56	4.38	4.36
CaO	8.32	9.03	8.10
MgO	3.38	3.57	3.20
Na_2O	0.95	1.05	1.05
K_2O	1.63	1.60	1.57
SO_3	1.70	1.87	2.22
Loss on Ignition	24.1	25.1	26.1
Ba (ppm)	310	306	283
Mn	602	568	508
Sr	309	333	302
Ti	2910	2560	2890

* Digested samples in mixture of acids, analyzed solution by inductively coupled Argon Plasma Spectrograph.

Carbon and Sulphur by Leco Induction Furnace

Analyses by Can-Test Ltd.

Table 5: Modified Fischer Assay of Oil Shales

	Shale Sample A					Shale Sample B	
Size Fraction (mm)	<0.5	.5-1.0	1-2	2-4	>4	0.5-1.0	1.0-2.0
Oil Yield (wt%)	5.2	5.5	7.8, 8.1 > 8.0	8.1, 7.6 > 7.85	7.6	2.9	4.5
Water Yield (wt%)	2.1	2.0	2.2, 2.3 > 2.25	2.2, 1.8 > 2.0	1.6	3.2	2.4
Gas Lost (wt%)	1.2	5.5	3.0, 1.6 > 2.3	1.7, 3.6 > 2.7	4.8	1.4	3.1
Char Yield (diff.)	91.5	87.0	87.0, 88.0	87.0, 88.0	86.0	92.5	90.0
Oil Yield (I.gal/ton)	12.1	12.7	18.0, 18.6	18.9, 17.4	17.4	6.7	10.4
Oil Density (g/ml at 15.5°C)	0.8562	0.8670	0.8670, 0.8678	0.8563, 0.8763	0.8752	0.8573	0.8634

Analysed at Research and Productivity Council, Fredericton

Table 6: Spouting of Oil Shale in Air at Room Temperature

Avg. Particle Size	[mm]	0.5-1.0	1.0-2.0	2.0-4.0
Spouting Velocity	[cm/s]	20.3	56.1	162.3
Eqv. Flowrate into Reactor	[L/s]	2.61	7.22	20.88
	[cfm]	5.53	15.28	44.25
Spout Quality (in terms of stability)		poor	good	good
Annulus Height above inlet	[cm]	16-Hm	45=Hm	30=/=Hm*

*(The maximum height Hm, was not reached due to the maximum available air flow rate)

The minimum spouting velocities at room temperature were measured in a half-cylindrical spouted bed to facilitate visual observation. The half-bed has similar dimensions as the reactor except its column diameter (=15.2 cm). The results are given in Table 6.

4. Procedure for Pyrolysis Experiments

The pyrolysis apparatus used in most of the tests was that of Figure 1, and Table 1. A photograph of the unit is shown in Fig. 3. Prior to successful runs being conducted, the electric preheater had to be completely re-built, and the main pyrolysis unit had to be removed from the furnace and new gaskets put in all joints. Because of settling of solids in the horizontal pipe upstream of the cyclone, an insert was installed to reduce the cross-sectional area available for flow.

The off-gas sampling train from which the oil yields were to be determined had to be completely re-built and the sampling location changed from that used for the previous studies on coal.

A new feed system had to be fabricated to handle the middle plus the coarse oil shale fractions.

The basic mode of operation with this pyrolysis is to change the empty reactor with inert solids, heat to temperature with air, switch the gas to N_2-CO_2 and feed oil shale into the sand bed over a 1-1 1/2 hour period. The oil shale accumulates in the bed during this period, and the off-gases are sampled continuously for oil. At the end of the run the bed materials and cyclone products are recovered. The oil yield is calculated from the oil recovered in the impinger train knowing the sampling rate and the total gas input.

a) Pyrolysis.

Spouting air was fed into the bed and the required amount of inerts

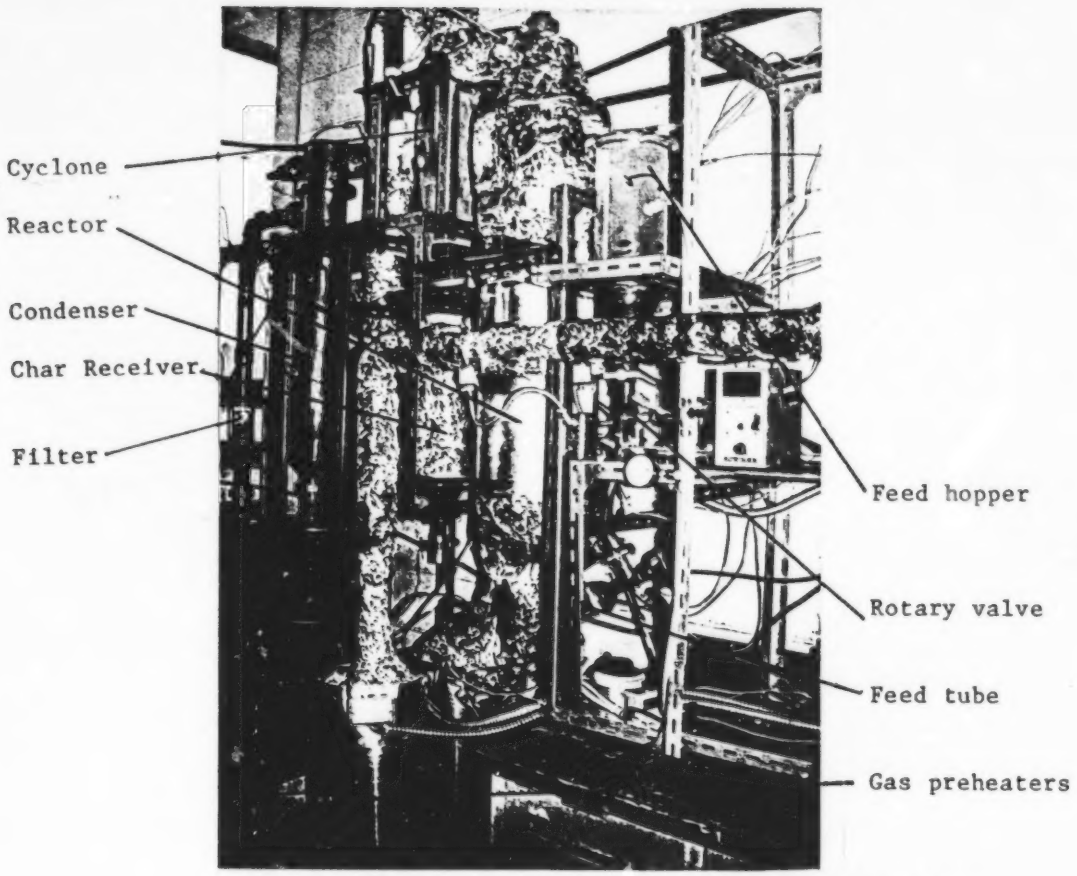


Fig. 3 Photograph of Electrically Heated Pyrolyzer

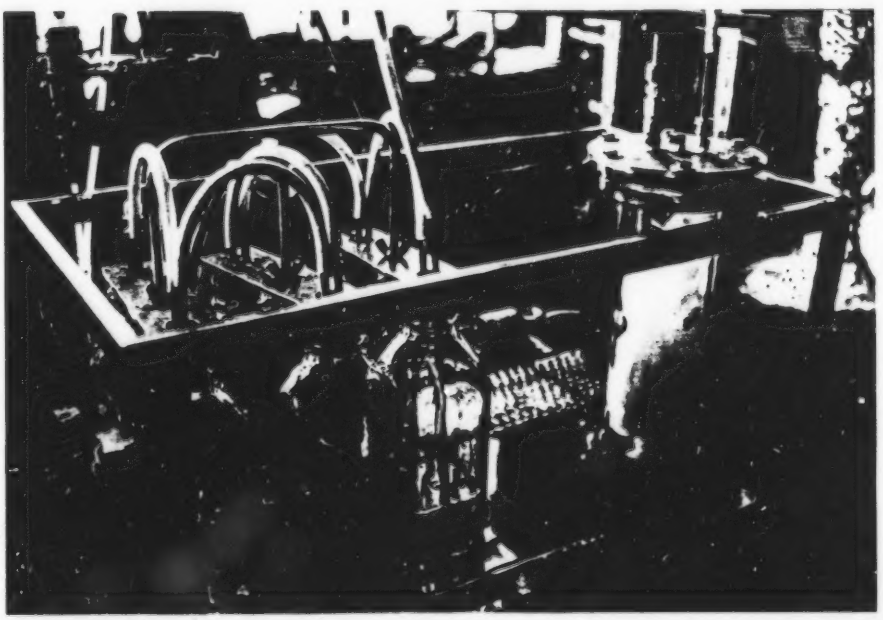


Fig. 4 Photograph of Impinger Train

(5.9 Kg Ottawa sand) was charged into the reactor. After re-installing the tube-sections of the sampling line that includes the ball-valve and after closing this valve, the electrical heaters were switched on. The assembly of the remaining parts including the impinger train was carried out during the heating-up period. Soon after the required temperature was reached, the air stream was replaced by a mixed-gas stream of CO_2 and N_2 (Volume ratio 15:85) and a period of 15 minutes was allowed to reach steady state condition. Thereafter, the impinger train was activated by opening the ball-valve followed by the extraction of a blank gas sample using a syringe. This sample was injected into a gas chromatograph; its result was used as reference reflecting zero feed-rate condition. The ball-valve was closed again to interrupt the isokinetic gas stream an the oil shale feed mechanism started (=zero time). Only after 5 minutes have passed, was the impinger train reactivated; a precaution to exclude the nonsteady state effects during the few initial minutes of feeding. Gas samples were extracted at respectively 15, 30, 45, 60, 75 and 80 minutes. Immediately after the last gas sample extraction, everything including the isokinetic gas stream was switched off, except the N_2 inlet gas stream to cool the system. The period between 5 to 80 minutes therefore accounted for the tar trapped in the impingers.

b) Preparation and Handling the Impingers for Iso-Kinetic Off-Gas Sampling.

A photograph of the impinger train is shown in Fig. 4.

The impingers, the interconnecting pipes and the tube-sections of the sampling line which connects to the main off-gas line were thoroughly cleaned, rinsed with solvents and dried before every experiment.

The first impinger was filled with glass wool to obtain a large

contacting surface for condensation and filtering effects. This helps to retain the heavier tar fractions.

The second up to fifth impinger was filled with a mixture of methylene dichloride and water (2:1 volume ratio). The sixth bottle contained methanol to trap the remaining tar-mist as well as entrained methylene dichloride. The last bottle contained water to trap any entrained methanol.

Care was taken to prevent a back-spill of methylene dichloride from the second impinger into the first one, as this would contaminate the gas-sample extracted through a septum just upstreams of the first impinger (high vapour pressure of methylene dichloride).

Therefore, these containers were interconnected only in the last minute before the sampling line was activated, and a slight vacuum was always maintained during an interruption. For the same reason, ice was added to the waterbath only after the start.

c) Post Experimental Run

The next day when the system was cooled off, the contents of the reactor and the cyclone were collected and weighed. Its difference with the Ottawa sand accounts for the char collected. The feed bin was also emptied to determine the feed rate and the absolute amount of oil shale fed. This was used as reference quantity. The glass wool in the main tar filter was replaced after each experiment. The impinger train and the whole sampling line were dismantled and washed with solvents to recover the tar. The washing solution was filtered to remove fine particles and separated from water by solvent extraction. This was followed by evaporation (55°C, 20 mm Hg) in a rotary vacuum evaporator to recover the tar. Any remaining trace of water was removed using sodium sulphate. The recovered tar was weighed for its yield.

Results of Pyrolysis Tests

Table B-1, Appendix B lists data from all tests.

a) Effect of Temperature on Oil Yield and Composition

There are two main temperatures involved in the spouted bed pyrolysis system - the temperature of the pre-heated gas as it meets the shale at the bed inlet, and the temperature of the spouted bed itself. Both of these temperatures may be expected to have some influence on the oil yield and quality depending on the relative rate of the devolatilization process and any subsequent degradation reaction of the oil such as cracking. Thus if the devolatilization is virtually instantaneous, oil would be released at the lower inlet temperature and subsequently be heated as it passes through the bed. If the devolatilization process is slow, the inlet temperature may be of lesser importance. In this study, the inlet and bed temperatures were matched within experimental error in nearly all cases for tests done in the electrically heated unit. One experiment was done with the inlet some 12°C below the temperature in the bed.

The temperature range covered was 454°C to 554°C and experiments were done on a single feed size of 1-2 mm, and at essentially constant feed rates of 1.3-15 kg/h. Table 7 lists the results. The oil yield is plotted versus temperature in Fig. 5 which shows the typical response for a pyrolysis process - a maximum in the oil yield at an optimum temperature. Thus at about 475°C, the oil yield reaches 7.1% which given the values of Table 5 represents 89% of the modified Fischer Assay yield. The plot suggests that possibly a higher yield can be achieved at a temperature slightly below 475°C. Run 6B which is slightly above a smooth curve through the rest of the results, was the one run where the inlet temperature was below that of the bed itself. Further work would show whether this effect is significant

Table 7: Effect of Temperature on Oil Yield and Composition

Expt No.	Temperature Bed (°C)	Inlet	Shale Feedrate (kg/h)	Oil Yield wt%	% Fischer Assay	Oil Analysis* (wt%) C	H	N	S	**	Atomic Ratio H/C
8	454	450	1.38	4.3	54.1	83.03	10.55	1.25		5.17	1.51
11	477	470	1.50	7.1	89.3						
4	503	503	1.56	5.8	73.0	81.47	10.70	1.02		6.81	1.57
5	501	501	1.33	6.3	79.3	82.46	10.66	1.13	0.63	5.12	1.54
6B	540	528	1.29	5.3	66.6	81.92	10.91	0.88		6.29	1.59
7	554	554	1.33	2.4	30.2	81.77	10.92	0.81		6.50	1.59

Particle size 1-2 mm * Microanalytical analysis ** Unaccounted

Table 8: Effect of Particle Size on Oil Yield and Composition

Expt No.	Particle Size Range (mm)	Shale Feedrate (kg/h)	Temperature Bed	Inlet °C	Oil Yield wt%	% of Fischer Assay	Oil Analysis (wt%) C	H	N	S	**	Atomic Ratio H/C
2	0.5-1.0	1.49	509	509	2.4	43.6	81.58	11.02	0.7		6.70	1.61
3		1.37	505	505	4.2	76.4	82.18	10.73	1.05		6.04	1.56
4	1-2	1.56	503	503	5.8	73.0	81.47	10.70	1.02		6.81	1.57
5		1.33	501	501	6.3	79.3	82.46	10.66	1.13	0.63	5.12	1.54
6A	2-4	1.25	507	518	7.4	94.3	82.73	10.66	1.14		5.47	1.54
10		1.20	506	505	7.1	90.4	82.64	11.35	1.12		4.89	1.64

** Unaccounted

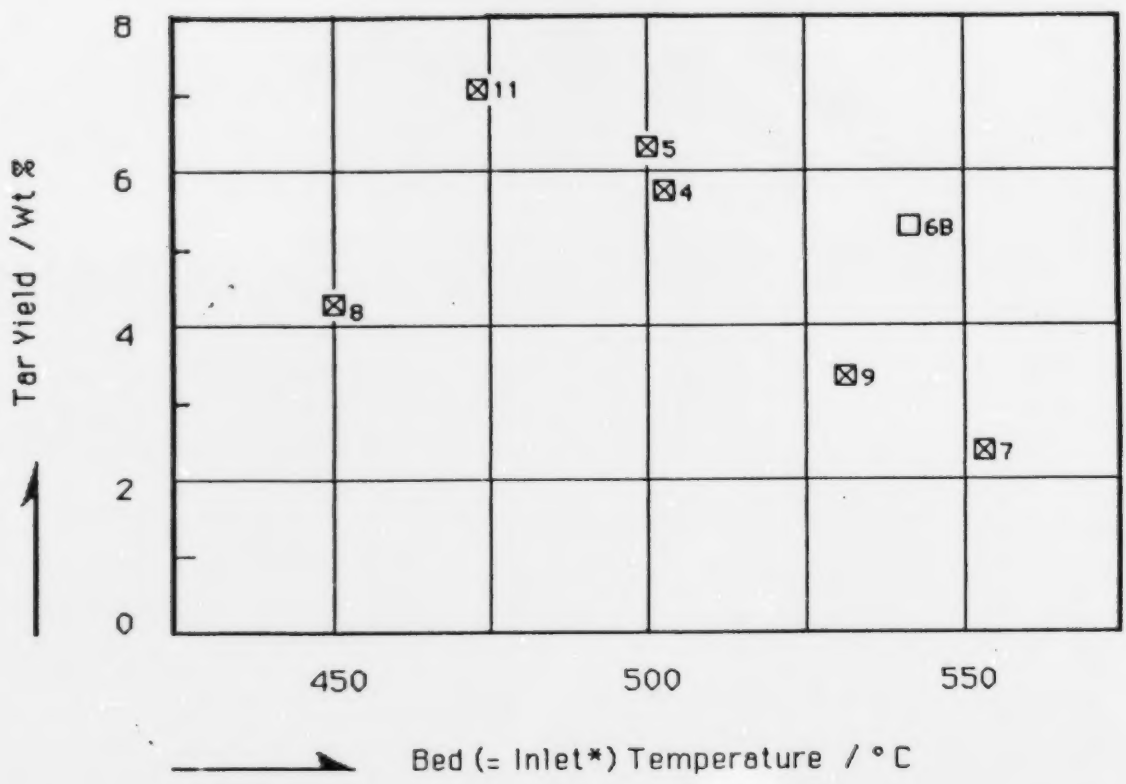


Fig. 5 Oil Yield as a Function of Temperature for 1-2 mm Oil Shale Particles (Bed temperature equal to inlet temperature except for experiment 6B)

or not at lower temperatures desired for higher oil yields.

The composition of the oils produced at different temperatures is also given in Table 7. Typical oils contain 81.5-83% C, 10.6-10.9% H, 1% N and 5-6.8% unaccounted. These oils may be enriched in oxygenated species due to the CO_2 used in pyrolyzing or contain traces of methanol or solent. Section 5(j) below describes attempts to resolve this problem. As the pyrolysis temperature increases, the atomic H/C ratio increases. At temperatures near the maximum oil yield H/C ~ 1.57. This value seems to be in agreement with expected values for shale oils produced by pyrolysis. Appendix C gives additional data on oil composition and typical boiling curves.

It should be noted that all these experiments were done using an initial bed consisting of silica sand, and with a pyrolyzing gas consisting of 15% CO_2-85% N_2. Runs 4 and 5 give an indication of the reproducibility of the oil yield results. This will be discussed further below.

b) Effect of Oil Shale Particle Size on Oil Yield and Composition

A series of runs was carried out at a fixed temperature of 506°C to investigate the effect of oil shale particle size. It will be evident from Fig. 5 that this temperature is somewhat above the optimum of 475°C for the 1-2 mm particles, however the curve of oil yield versus temperature is not too steep in this region. Figure 6 shows the plot of oil yield versus mean particle size and Table 8 summarizes the results. It should be recognized that the mean size is being plotted here, and that for the largest particles of 3 mm, for example, there is a distribution of sizes within the range 3 ± 1 mm. The trend towards higher yields with increasing size is unmistakeable, with each size having been tested in duplicate, however the explanation of the results is open to question. In coal pyrolysis, the usual trend is opposite to that of Fig. 6 and the common explanation is that

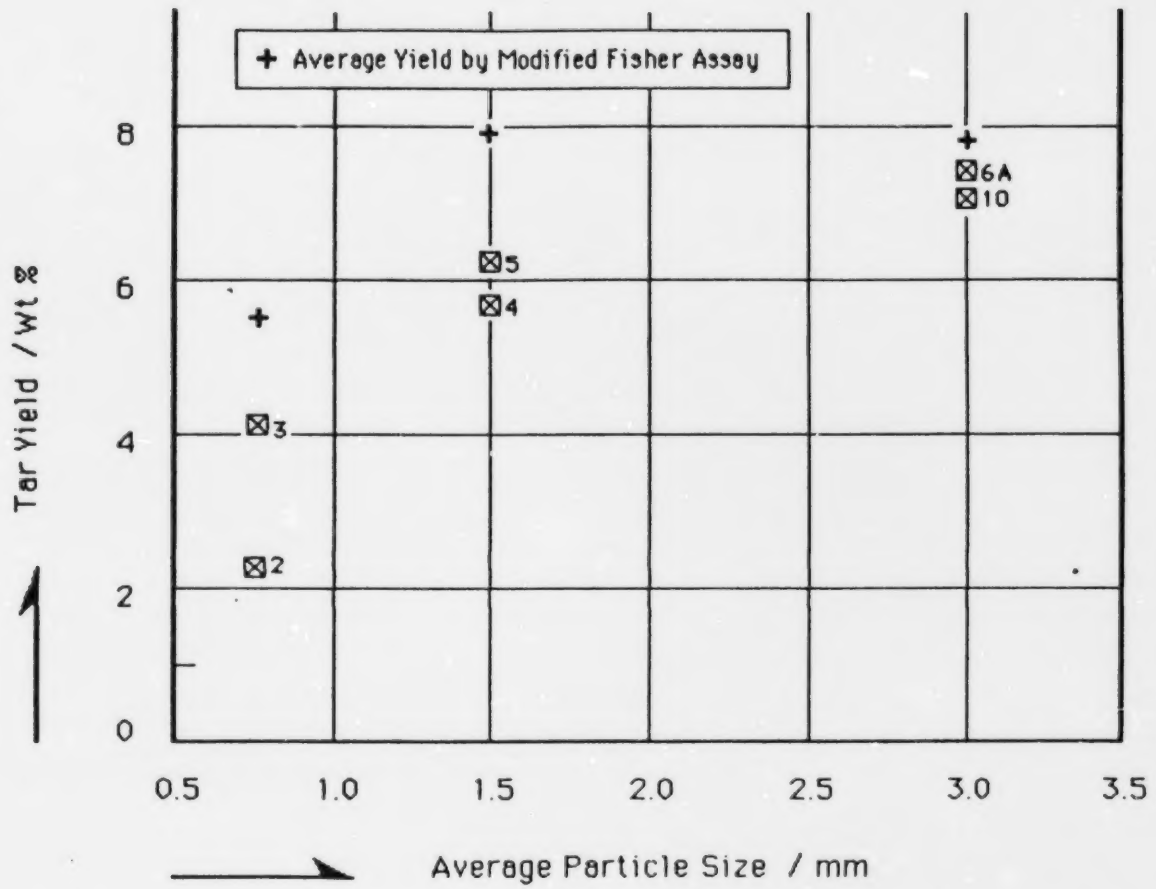


Fig. 6 Oil Yield as a Function of Average Oil Shale Particle Size (Bed temperature equal to inlet temperature of 506°C)

for smaller particles the pyrolysis is more rapid, and the opportunities for tar consuming reactions such as polymerization and deposition within the particle is reduced. In the present case it may be that these liquid consumption reactions are negligible and that the larger particles where internal temperature gradients exist are actually releasing oil at a lower temperature than the smaller particles. If this is so, a different curve would be expected at 475°C than at 506°C. Clearly there is room for some optimization here, and further tests at lower temperatures for the larger oil shale particles are in order.

The Fischer Assay values are also plotted in Fig. 6 from which it is evident that the ratio of oil yield/Fischer Assay oil yield also increases with particle size. It is evident that the smaller oil shale particles have a smaller potential oil yield. For the coarsest particles yields of 90-94% of the Fischer Assay values were obtained. With the coarser feed, some segregation should be expected in the spouted bed, as the inert silica bed material was kept at 1.1 mm.

The composition of the produced oils are given in Table 8. As particle size increases there is no consistent trend among the three samples analyzed. The atomic H/C ratio is highest and the unaccounted for lowest for the oil produced from the coarser 2-4 mm shale.

c) Effect of Oil Shale Feed Rate on Oil Yield and Composition

The feed rate used in the experiments on temperature and particle size effects was held constant at about 1.4 kg/h which corresponds to a mass throughput based on the cross-sectional area of the reactor of 0.03 kg/m^2s. Tests were done with the coarsest feed at three different feedrates, as shown in Table 9 and Figure 7. There is a strong linear decrease in oil yield with feed rates. As a percent of Fischer Assay values the drop is

Table 9: Effect of Feedrate on Oil Yield and Composition

Expt No.	Temperature Bed °C	Temperature Inlet °C	Shale Feedrate kg/h	Oil Yield % wt	Oil Yield % of Fischer Assay	Oil Analysis (wt%) C	H	N	Unaccounted	Atomic Ratio H/C
10	506	505	1.2	7.1	90.5	82.64	11.35	1.12	4.89	1.46
12A	506	502	1.94	4.5	57.3	83.65	10.77	1.23	4.35	1.53
12	506	502	2.71	2.0	25.5	83.42	10.89	1.29	4.40	1.56

Oil shale size range 2-4 mm.

Table 10: Effect of Pyrolyzing Gas Composition

Pyrolyzing Gas	85% N_2 - 15% CO_2		100% N_2
Expt. No.	4	5	14
Temperature (Inlet/Bed) °C	503/503	501/501	491/500
Feed Rate (kg/h)	1.56	1.33	1.35
Oil Yield (%wt)	5.8	6.3	3.4%
(% Fischer Assay)	73.0	79.3	42.8
Oil Analysis (%wt)			
C	81.47	82.46	82.49
H	10.70	10.66	10.89
N	1.02	1.13	1.17
S	-	0.63	0.75
Unaccounted	6.81	5.12	4.70
Atomic H/C Ratio	1.57	1.54	1.57

* Shale size 1-2 mm.

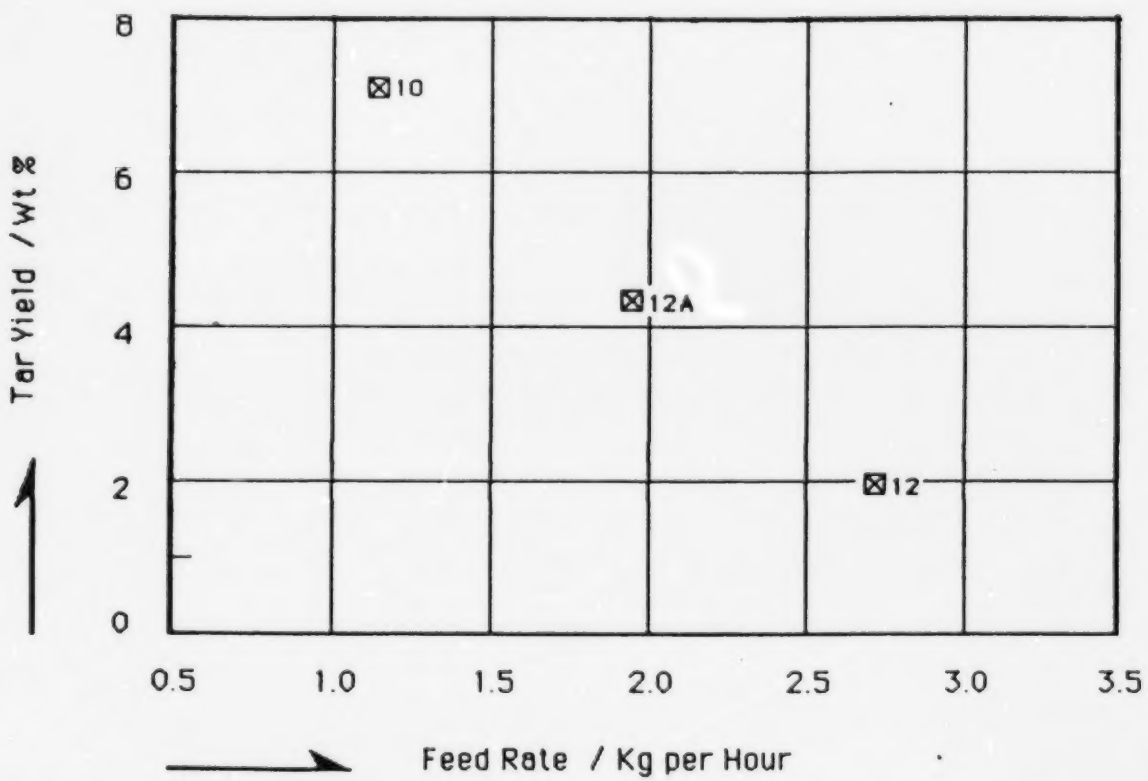


Fig. 7 Oil Yield as a Function of Feed Rate for 2-4 mm Oil Shale Particles (Bed temperature equal to inlet temperature of 505°C).

from 90.5 to 25.5%. A marked decrease in liquid yield with feed rate has also been found in coal pyrolysis, where the decrease has been attributed to secondary reactions on the hot char which accumulates in the bed. In the present case, the same factor may operate as the spent shale accumulates in the bed with time. The reactor does not operate in a true steady state vis a vis composition of the bed material. This will be discussed further below where the solid yield, and bed composition will be described in detail.

The oil composition data is given in Table 9. As the oil yield falls off, the hydrogen content decreases, but the hydrogen/carbon atomic ratio remains at about 1.5 ± .05.

d) Effect of Bed Material

Due to time constraints which arose as a result of a series of equipment failures, this variable was not studied in detail. Three runs with spent shale as bed material were done in the two-stage unit, and are described in Section 5(f). The experimental work on the single stage unit is being continued by T. Tam funded from other grants and a supplemental note on the effect of bed material will be written.

e) Effect of Pyrolysing Gas

One trial was done in nitrogen rather than the 85% nitrogen -15% CO_2 mixture. Results are shown below in Table 10 in which a direct comparison of these two conditions is made. The oil yield in nitrogen seems low, but no valid conclusion can be drawn until the experiment is repeated. Two useful observations can be made however. The first is that no CO_2 was observed in the off-gas. This has some implications for the calculation of gas yield in runs where CO_2 was used in the pyrolyzing gas. The other is that in the product oil, the unaccounted fraction (oxygen) is only slightly lower than in the case of CO^2 pyrolysis. Thus it appears that the oxygen

Table XI Data from Pyrolyzer/Combustor tests

	LOWER STAGE								
Run no.	Feed Rate (kg/h)			Gas Composition					T_{max} °C
	Propane	Air	Steam	CO_2	CO	N_2	H_2	CH_4	
30-1	1.57	14.16	8.70	9.5	5.4	78.6	6.2	0.0	999
30-2	1.57	13.02	8.70	9.8	6.2	76.4	7.5	0.0	1011
30-3	1.57	15.66	8.70	11.1	3.0	78.2	3.8	0.0	1037

UPPER STAGE									
Bed Composition	T °C	Gas Composition					Oil Shale" Rate (kg/h)	Char Yield %	Tar Yield %
		CO_2	CO	N_2	H_2	CH_4			
Oil Shale	474	10.3	4.7	79.2	5.5	0.0	4.08"	-	4.07
|	501	10.1	6.0	76.2	7.4	0.0	4.08"		3.84
Oil Shale	530	13.0	2.3	80.9	3.6	0.0	4.08"		4.04

Table 12: Spent Shale Properties and Yield

Run	3		4		10	
Temperature						
Particle Size	0.5-1.0 mm		1-2 mm		2-4 mm	
	Bed Shale	Cyclone Catch	Bed Shale	Cyclone Catch	Bed Shale	Cyclone Catch
Total carbon(%wt)	4.91	6.84	4.64	6.87	5.33	5.89
Organic carbon(%)	3.48	4.77	2.37	4.30	2.36	3.20
SiO_2(%wt)	56.7	61.2	51.6	52.4	50.3	59.8
Al_2O_3	16.6	9.33	14.5	11.2	13.1	8.81
Fe_2O_3	10.1(?)	3.96	5.66	4.80	5.52	3.84
CaO	3.34	6.54	9.30	8.77	10.9	7.42
MgO	2.24	2.50	3.97	3.45	4.28	2.93
Na_2O	1.35	0.95	1.26	1.31	1.38	1.10
K_2O	2.64	1.58	2.23	1.83	2.17	1.55
Ba (ppm)	440	373	390	373	376	300
Mn	790	402	690	570	705	446
Sr	175	290	340	368	385	310
Ti	3960	2440	3430	2970	3180	2340

does not arise from the CO_2. (See Section 5(j) below).

(f) Tests in the Two-Stage Unit with Oil Shale B

Three oil-shale tests were carried out by visiting professor Dr. G. Rovero in the two-stage combustor/pyrolyzer shown in Fig. 2. Here no electrical heating is used, rather the shale is pyrolyzed in combustion gases. In this case for ease of operation the lower combustion stage was operated on propane rather than spent shale. The combustion was carried out under reducing conditions to protect the oil produced in the pyrolysis stage from oxidation. This unit operates in a true steady state with a bed overflow in the upper stage so that a mean residence time can be evaluated. In addition, no sand was used - the upper bed consisted of spent shale. The tests were carried out at a time when only Oil Shale B was available. This shale had a significantly lower potential oil yield (Table 5) than Oil Shale A.

Table 11 outlines the results of these tests. Of note is the fact that the oil yields average about 4%, which are 89% of the modified Fischer Assay values for this oil shale. These yields were achieved at an oil shale feed rate of 4.1 kg/h. Fig. 7 would imply that much lower oil yields would be expected, so the results for these tests are indeed promising. These better results may possibly be due to the presence of about 6% hydrogen and an equivalent amount of carbon monoxide in the pyrolyzing gas.

g) Gas Yields

Gases were analyzed by chromatography. Species identified in the off-gases were H_2, CH_4, C_2H_4, C_2H_6, C_3H_8 and C_4H_{10}. All the above gases were present in very how yields typically as follows: H_2 0.05%, CH_4 0.09%, C_2H_4 0.08%, C_2H_6 0.07%, C_3H_8 0.4%, C_4H_{10} 0.3%. These total about 1%. Because CO^2 ws used in the pyrolyzing gas at the level of 15% its yield could not be

determined with accuracy because of fluctuations of the gas inlet flowrate. Surprisingly with the run done with nitrogen as a pyrolyzing gas virtually no CO_2 appeared to be produced. The Fischer Assay gas yields are about 1.2-5.5%, (Table 5) however in the rapid pyrolysis experiments the upper range of these values were not reached. Whether this is due to CO_2 or not remains to be resolved.

h) Spent Shale Composition and Overall Mass Balances

The compositions of spent shales found in the bed and recovered from the cyclone catch from three runs of different particle size are given in Table 12. On balance it can be seen that the cyclone catch contains higher carbon content than does the bed material. Thus material which leaves the bed by attrition and carryover is generaly incompletely reacted compared with that which remains in the bed. The smaller amount of fines produced with coarse feed may contribute to the higher oil yield noted in Fig. 6.

Overall mass balances were not closed except by calculation because of the substantial losses of fine materials through the cyclones. However mass balances using several species present in the shale, the bed material and the cyclone catch, (Sr, Ba, Ti, Fe_2O_3), all showed that the uncollected material which passed through the cyclone was about one-third of the oil shale feed. This points up a major consideration that would have to go into any planned rapid pyrolysis process based on the spouted bed - the need for removal of dust from the gas, and perhaps a recycle from the primary cyclone. Attrition of the solids is thus a very significant problem. This was evident initially from the behaviour of the oil shale sample on crushing where large amounts of fines were found to be produced and was confirmed in the pyrolysis trials by the large amount of fines which passed through the cyclone. It should be noted that the cyclone is oversized and was not

expected to give particularly efficient collection.

i) Thermogravimetric Analyses of Oil Shales

Weight loss data were generated for the oil shale using about 10 mg samples heated in a nitrogen atmosphere in a thermogravimetric apparatus. Figures 8a-c show typical thermograms. Common features of samples prepared from the three size ranges are:

(i) The beginning of the weight loss occur at temperatures of about 300°C.

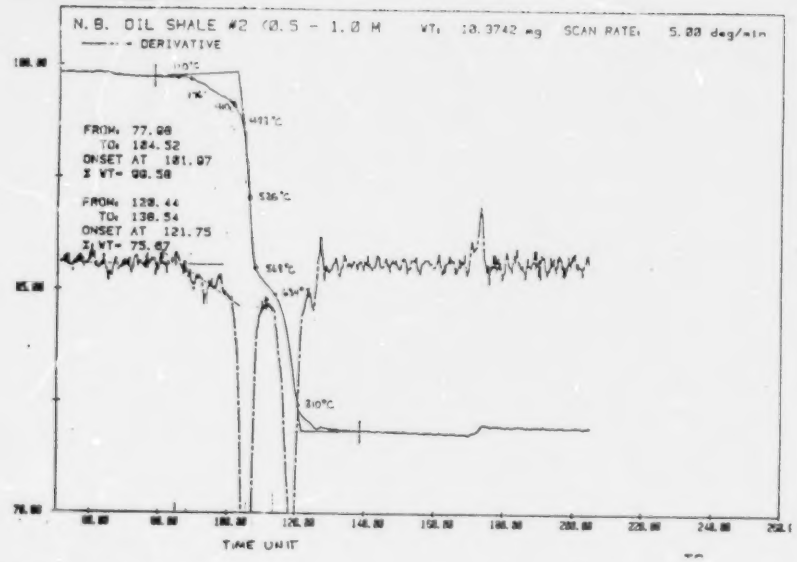
(ii) The maximum rate of weight loss occurs at about 520°C.

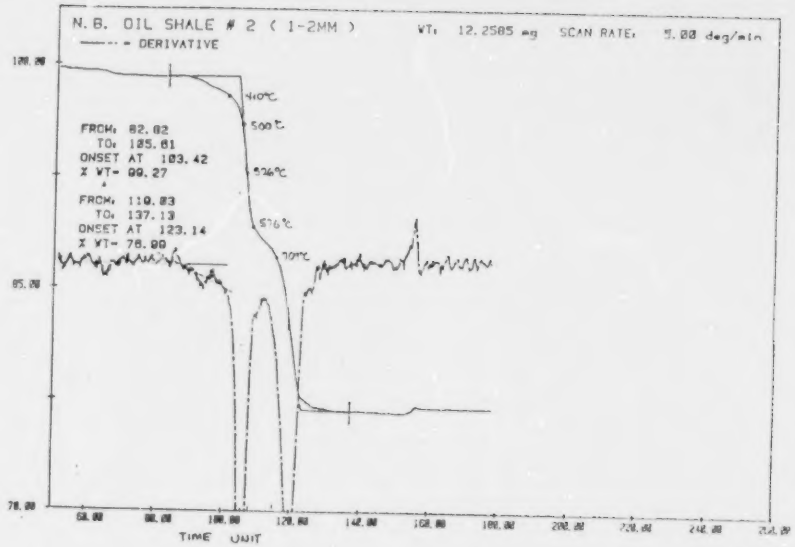
(iii) The organics are apparently expelled by about 700°C.

(iv) A secondary decomposition occurs above 750°C which is presumably the breakdown of carbonates.

j) Unaccounted for Species in Oils

An attempt was made to identify the unaccounted for species present in the oils. These species amount to about 4-5%. Work by others suggested that the oils from shale pyrolysis do not contain oxygen at levels over 1%, so it was thought that perhaps some methanol or methylene chloride from the solvent train might have contaminated the products. A solution of the oil was made in ethylbenzene and 1 μL was injected into a 50-m long DB5 capillary column in a chromatograph (See Appendix C). The resulting trace showed no methanol and no methylene chioride to be present. Alkene and alkane series up to about C_{30} were detected. The unaccounted species in Tables 7, 8 and 9 thus are still unidentified. As a precaution against being overly optimistic about the oil yields in the present experiments, it may be advisable to assume that the yields be corrected by multiplication by 0.95 in case the as yet unidentified species turns out to be a useless contaminant.





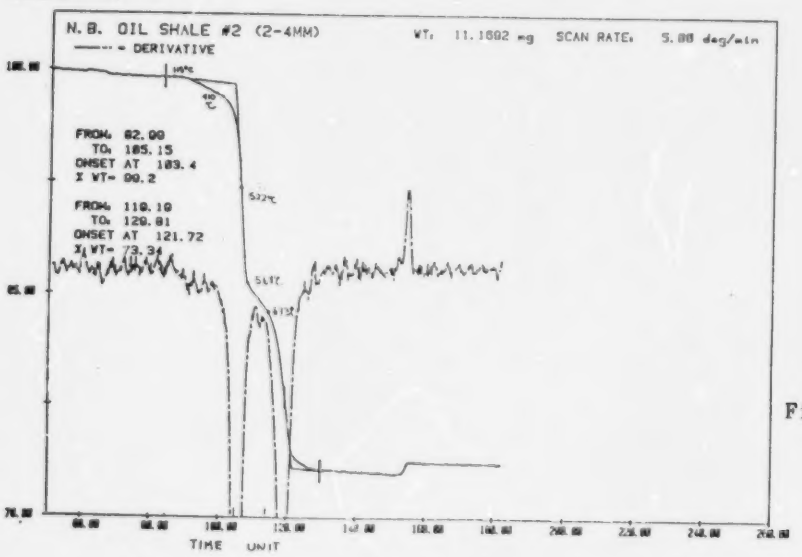


Fig. 8 Thermogravimetric Curves for Three Sizes of Oil Shale

6. Conclusions

This set of experimental studies has shown:

(i) New Brunswick oil shales can be pyrolyzed in a continuous feed spouted bed to give oil yields approaching 90% of the Fischer Assay.

(ii) For 1-2 mm sized particles, the optimum temperature for pyrolysis is around 475°C, above which oil yields fall off.

(iii) As the particle size is increased from 0.5-1.0 mm to 3-4 mm, the oil yield increased at a given feed rate and temperature.

(iv) Increases in feed rate of oil shale above the 1.5 kg/h value used in most experiments causes a decrease in oil yield. Tests in a two-stage unit where the pyrolyzing gas contains H_2 and CO showed high yields up to feed rates of 4 kg/h.

(v) There is a considerable amount of attrition in the spouted bed pyrolyzer which leads to production of fine dust.

(vii) The oil produced had H/C atomic ratios of about 1.57. Some 4% of the oil was not accounted for as C, H, S, N or solvents methanol or methylene chloride. Thermogravimetric analysis - simulated distillation showed that about fifty wt.% of the oil boils below 370°C and ninety wt.% below 510°C.

APPENDIX «A»

STATEMENT OF WORK

Objective:

To establish the chemical composition and yield of liquid products obtained by rapid pyrolysis of the oil shale from Albert formation in the province of New Brunswick, using the spouted bed technology.

To determine the effects of temperature, particle size and feeding rate on yields and chemical composition of liquid products, and to compare the inert silica and spent shale as the bed materials.

To compare the results obtained during the rapid pyrolysis with those obtained during retorting in the Fischer assay and hydrogen retorting in the pyrochem retort.

The above outlined objectives will be achieved by completing the following tasks:

Task 1

Obtain the sample of oil shale (≈ 500 kg) from the Albert formation in New Brunswick.

The preparation of the sample will include the crushing and sizing to obtain three different size fractions, i.e., 0.5-1.0 mm, 1.0-2.0 mm and 2.0-4.0 mm.

Task 2

Determination of the minimum spouting velocity for each size fraction at room temperature.

Perform the inital retorting trials according to the following procedure:

- charge the reactor with inert silica and turn on the air to reactor, steam to preheater and power to heater.
- replace the air by an 80:20 N_2-CO_2 mixture as soon as the temperature reaches 500°C.
- when the temperature reaches 600°C start feeding the oil shale at about 1.5-2.0 kg/hr rate.
- as soon as the steady state is reached start to collect the condensible volatiles for one hr and analyse gases by gas chromatography.
- determine total gas flow.
- determine the boiling range of the liquid products and analyse for C,H,N,S and O.

This procedure will be applied to each size fraction, i.e., total of three experiments will be performed.

Task 3

To determine the effects (either catalytic or inhibitive) of the spent shale, perform one experiment (intermediate size fraction) with the combusted spent shale as the bed material.

Task 4

If no inhibitive effects observed in the Task 3, use the spent shale as bed material and perform four experiments (400°, 500°, 600° and 700°C) using the intermediate size fraction.

Task 5

Perform the experiment with each size fraction of the sample at the optimal temperature (determined in the Task 4); i.e., total of three experiments.

Task 6

Establish the effects of feed rate at the optimal temperature and particle size fraction (determined in Tasks 4 and 5); i.e., perform the experiment at the feeding rate of 0.5, 1.0, 2.0 and 3.0 kg/hr.

Task 7

Tabulation and interpretation of the experimental results, preparation of final report.

APPENDIX B TABLE B-1 RESULTS FROM ELECTRICALLY HEATED PYROLYSER

EXPT. NO.	SHALE FEED SIZE (mm)	SHALE FEED RATE (kg/h)	TEMPERATURE (°C) WALL	TEMPERATURE (°C) BED	OIL YIELD WT%	OIL YIELD % FISCHER ASSAY	OIL ANALYSIS (WT %) C	H	N	S	UN.*	OIL H/C ATOMIC RATIO	SOLIDS** RECOVERED (%)
2	0·5 - 1·0	1·49	509	509	2·4	43·6	81·58	11·02	0·7		6·70	1·61	59·9
3	0·5 - 1·0	1·37	505	505	4·2	76·4	82·18	10·73	1·05		6·04	1·56	60·4
4	1·0 - 2·0	1·56	503	503	5·8	73·0	81·47	10·70	1·02		6·81	1·57	55·3
5	1·0 - 2·0	1·33	501	501	6·3	79·3	82·46	10·66	1·13	0·63	5·12	1·54	58·7
6A	2·0 - 4·0	1·25	518	507	7·4	94·3	82·73	10·66	1·17		5·47	1·54	57·8
6B	2·0 - 4·0	1·29	528	540	5·3	67·5	81·92	10·91	0·88		6·29	1·59	
7	1·0 - 2·0	1·33	554	554	2·4	30·0	81·77	10·92	0·81		6·50	1·59	62·7
8	1·0 - 2·0	1·38	450	454	4·3	53·8	83·03	10·55	1·25		5·17	1·51	61·0
9	1·0 - 2·0	1·40	530	550	3·3	41·3	83·12	10·84	1·16		4·88		60·9
10	2·0 - 4·0	1·20	505	506	7·1	90·4	82·64	11·35	1·12		4·89	1·64	68·4
11	1·0 - 2·0	1·50	470	477	7·1	89·3							
12A	2·0 - 4·0	1·94	502	506	4·5	57·3	83·65	10·77	1·23		4·35	1·53	61·4
12	2·0 - 4·0	2·71	502	506	2·0	25·5	83·42	10·89	1·29		4·40	1·56	66·8
14	1·0 - 2·0	1·35	491	500	3·4	42·8	82·49	10·89	1·17	0·75	4·70	1·57	

GAS FLOWRATE 254 std. LITERS/MIN. 15% CO_2 - 85% N_2 except EXPT. 14 100% N_2

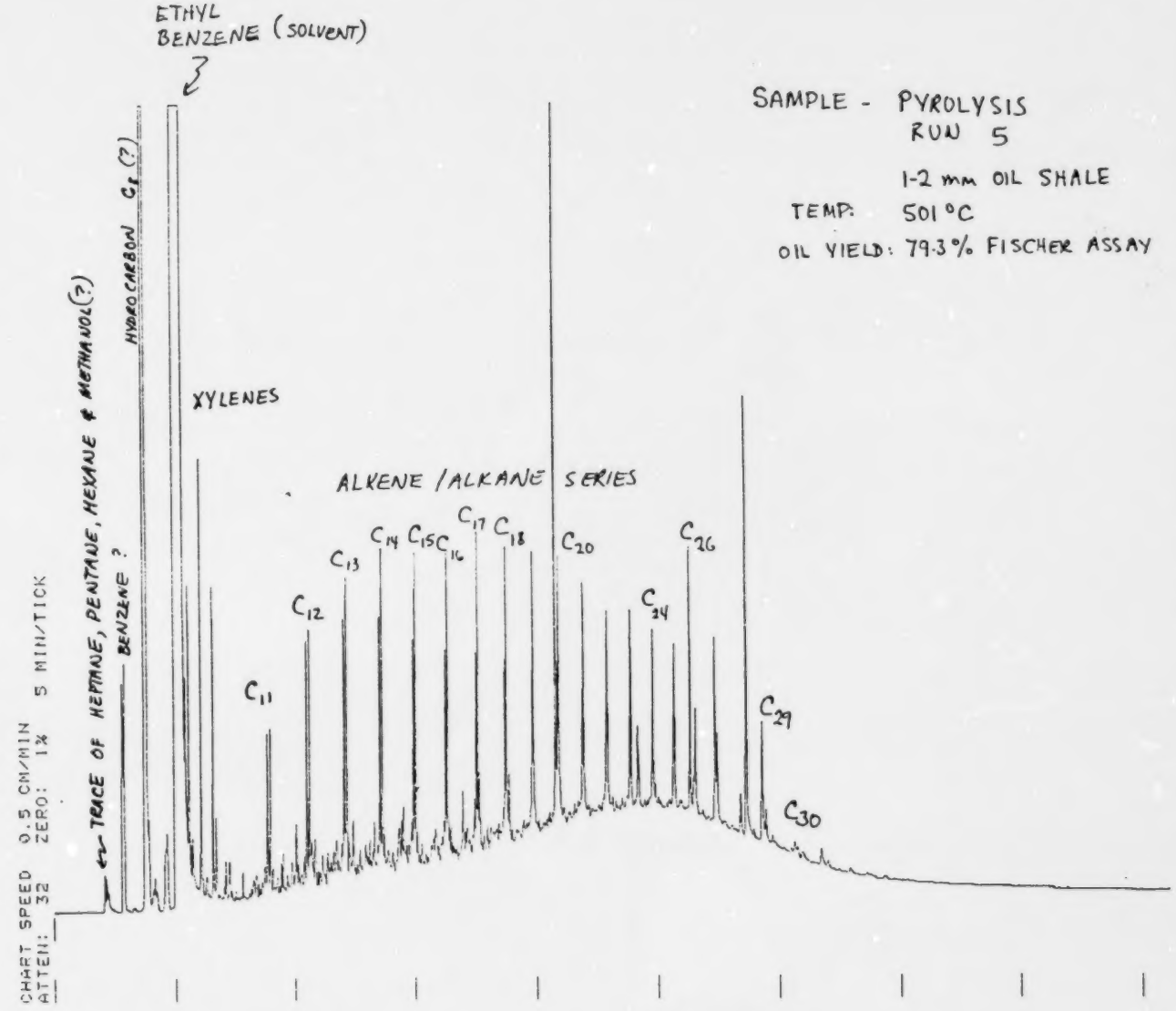
* UN. = 100 - (C + H + N + S) UNACCOUNTED FOR

** SOLIDS RECOVERED = (WT. CYCLONE CATCH + SHALE IN BED)/SHALE FED

APPENDIX C - Oil Characterization and Boiling Point Curves

A preliminary characteriztion of the oils was undertaken by Dr. K.C. Teo primarily to determine if solvent contamination by methanol or methylene chloride could have contributed to the fraction of the oil unaccounted for by elemental C, H, N and S analysis (See Section 5(j)). A trace from the capillary column gas-chromatograph shown as Fig. C-1 indicates the presence of ethylbenzene the solvent for the G-C, and no trace of either methanol or methylene chloride. The alkene-alkane series from C_{11} to C_{30} are clearly present, as well as some xylenes. Evaporation of the solvent (Section 4c) undoubtedly causes some losses of the very lowest molecular weight species.

Simulated distillation using a thermogravimetric method was used to obtain boiling point curves. This method was developed by K.C. Teo under contract 24 ST.23440-4-9074 and is described in a Final Report dated June 1985. The method involves heating milligram quantities of oil in a narrow tube in a thermogravimetric analyzer under nitrogen at atmospheric pressure and measuring the weight loss of oil distilled versus temperature. While the method must be considered tentative at this stage due to decomposition of the oil at high temperatures, it has been successfully calibrated against petroleum mixtures. Results for three shale oils are shown in Fig. C-2. Fifty % by weight of the oils boil below about 370°C, and 90% below about 510°C. A residue of 7-9.3 wt.% remained at T > 590°C.



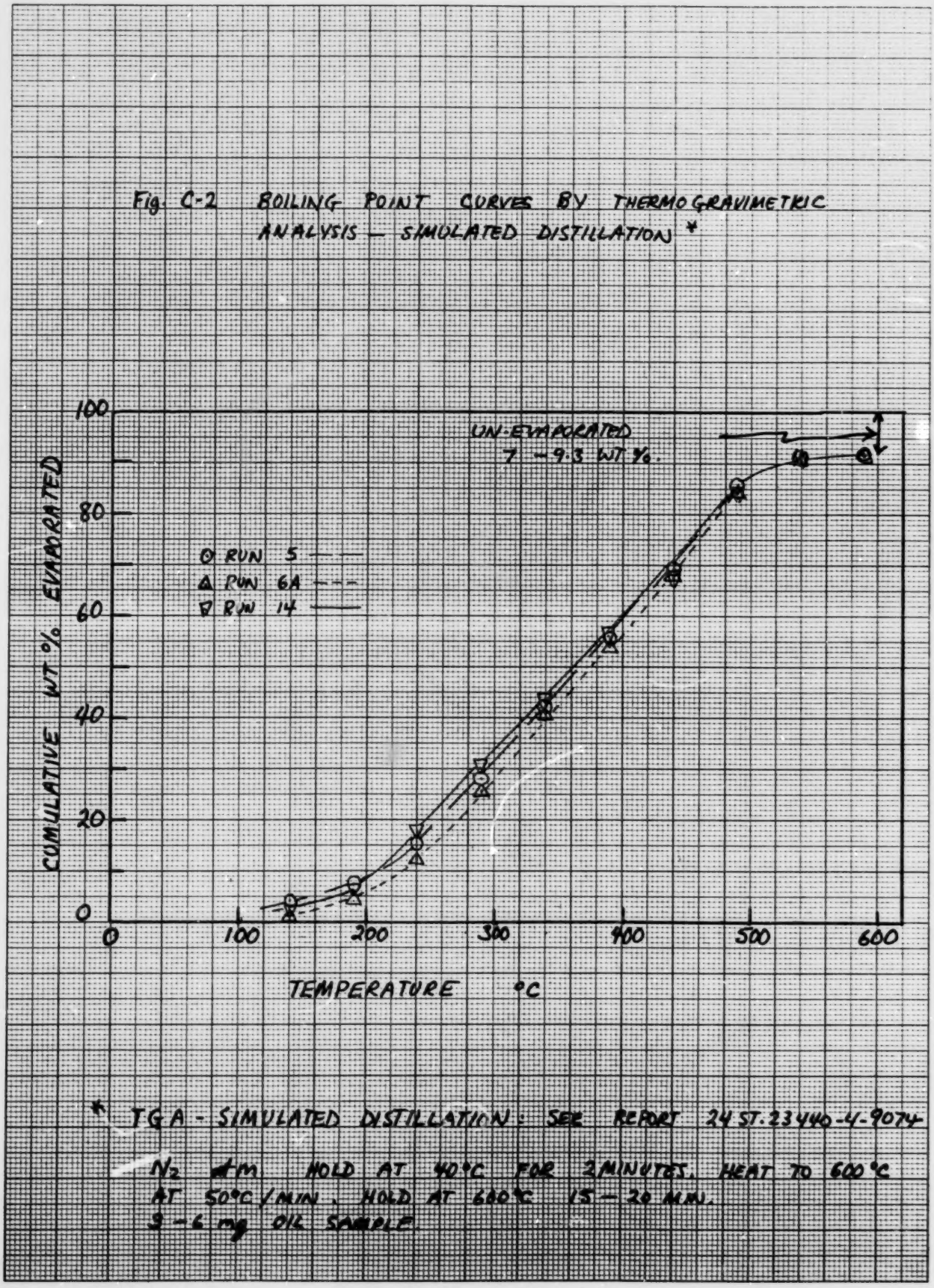
NOTES:
CAPILLARY (DB5) FID ON A-SIDE
SN=5 : T%=5 : WI=4
TEMP PR: 60°C(2')-R=5°C/'-300°C

Fig. C-1 CAPILLARY COLUMN CHROMATOGRAM FOR OIL FROM RUN 5.

461510

K•E 10 X 10 TO THE CENTIMETER 18 X 25 CM. KEUFFEL & ESSER CO. MADE IN U.S.A.

Fig. C-2 BOILING POINT CURVES BY THERMOGRAVIMETRIC ANALYSIS — SIMULATED DISTILLATION *



* TGA - SIMULATED DISTILLATION: SEE REPORT 24 ST. 23440-4-9074

N_2 atm HOLD AT 40°C FOR 2 MINUTES. HEAT TO 600°C AT 50°C/MIN, HOLD AT 600°C 15 - 20 MIN.
3 - 6 mg OIL SAMPLE.